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14. ABSTRACT
The term microbiologically influenced corrosion (MIC) is used to designate corrosion due to the presence and activities of microorganisms, ie, those organisms that cannot be seen individually with the unaided human eye, including microalgae, archaea, bacteria, and fungi. Microorganisms can accelerate rates of partial reactions in corrosion processes or shift the mechanism for corrosion. Microorganisms can influence pitting, dealloying, enhanced erosion corrosion, enhanced galvanic corrosion, stress corrosion cracking, and hydrogen embrittlement. Microbiologically influenced corrosion has been reported for all engineering metals and alloys with the exception of predominantly titanium and high chromium -nickel alloys. It has been documented for metals and nonmetals exposed to seawater, freshwater, distilled/demineralized water, crude and distillate hydrocarbon fuels, process chemicals, foodstuffs, soils, human plasma, saliva, and sewage. The following sections describe the estimated costs of MIC, mechanisms, and causative microorganisms contributing to MIC; techniques for diagnosing, measuring, and monitoring; engineering practices that influence MIC and strategies to prevent or mitigate MIC.

15. SUBJECT TERMS
corrosion; MIC; microbiologically influenced corrosion; alloys

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MICROBIOLOGICALLY INFLUENCED CORROSION

1. Introduction

The term microbiologically influenced corrosion (MIC) is used to designate corrosion due to the presence and activities of microorganisms, ie, those organisms that cannot be seen individually with the unaided human eye, including microalgae, archaea, bacteria, and fungi. This corrosion occurs in environments that can support the growth of microorganisms, including environments where corrosion would not be predicted (eg, low chloride waters) and the rates can be exceptionally high. According to a recent survey, damage due to corrosion in the United States is estimated at 276×10^9 dollars per year (1). Similar surveys in the United Kingdom, Japan, Australia, and Germany estimate the cost of corrosion to be 1–5% of the gross national product (2). Microbiologically influenced corrosion is reported to account for 20% of the total cost of corrosion (3). Original case histories of MIC have been published in peer-reviewed journals, symposia proceedings, edited collections (4–7) and books (8–10).

2. Microorganisms

The microorganisms involved in microbiologically influenced corrosion are from all three main branches of evolutionary descent, ie, archaea, bacteria, and eukaryotes (Fig. 1). Archaea and bacteria are prokaryotes and have no cell nucleus or any other organelles within their cells. In the past archaea, were viewed as an unusual group of bacteria and named archaebacteria, but since the archaea have an independent evolutionary history and show many differences in their biochemistry from other forms of life, they are now classified as a separate domain in the three-domain system.

2.1. Prokaryotes *Bacteria.* Bacteria have received the most attention for their influence on corrosion. Bacteria can be subdivided into groups depending on shape (eg, rods, cocci, and filaments), requirements for oxygen (aerobic or anaerobic), source of energy (eg, heterotrophic, autotrophic), or type of preferred anaerobic electron acceptor (eg, sulfate-, nitrate-, iron-, and chromate-reducing). Bacteria may exist individually, but tend to form colonies, reproducing by binary fission or cell division. Individual cells vary in size, depending on species and environmental conditions. In nutrient-deprived waters, dwarf cells can form. Obligate aerobes require oxygen for survival and growth. Microaerophilic bacteria require low oxygen concentration and facultative anaerobic bacteria can grow under aerobic or anaerobic conditions. Obligate anaerobic microorganisms cannot grow in the presence of oxygen. Obligate anaerobic bacteria are, however, routinely isolated from oxygenated environments associated with particles, crevices, and most importantly, in association with other bacteria that effectively remove oxygen from the immediate vicinity of the anaerobe. In aerobic respiration, energy is derived when electrons are transferred to oxygen, the terminal electron acceptor. Facultative anaerobes can use oxygen or a variety of organic and inorganic compounds including sulfate, nitrate, nitrite, carbon dioxide, Fe^{3+}, Mn^{4+}, and Cr^{6+}. Heterotrophic bacteria derive energy from a wide range of

organic molecules while autotrophic bacteria oxidize inorganic compounds, as sources of energy. When both autotrophic and heterotrophic mechanisms operate simultaneously the metabolism is mixotrophy. Phototrophic bacteria can use light as a source of energy.

Archaea. Archaea are a group of single-celled microorganisms. Generally, archaea and bacteria are quite similar in size and shape, although a few archaea have very unusual shapes, eg, the flat and square-shaped cells. Despite the visual similarity to bacteria, archaea possess genes and several metabolic pathways that are more closely related to those of eukaryotes. The archaea exploit a much greater variety of sources of energy than eukaryotes: ranging from familiar organic compounds (eg, sugars), to using ammonia, metal ions, or even hydrogen gas as nutrients. Archaea reproduce asexually and divide by binary fission, fragmentation, or budding; in contrast to bacteria and eukaryotes, no species of archaea are known that form spores.

2.2. Eukaryota. The cells of eukaryotes possess a clearly defined nucleus, bounded by a membrane, within which deoxyribonucleic acid (DNA) is formed into distinct chromosomes. Eukaryotic cells also contain mitochondria and other structures that, together with a defined nucleus, are lacking in the cells of prokaryotes. Typically, eukaryotic cells are 10 times larger in each dimension than bacteria and archaea. Fungi are eukaryotic organisms. Yeasts, molds, and mushrooms are examples of fungi. The majority of species grow as multicellular filaments called hyphae forming a mycelium; some fungal species also grow as single cells. Sexual and asexual reproduction of the fungi is commonly via spores, often produced on specialized structures or in fruiting bodies.

Microorganisms require water, nutrients, and electron acceptors. Liquid water is needed for all forms of life and availability of water influences distribution and growth of microorganisms. The major elements required for a typical microorganism composition is as follows: $C_{169}(H_{280}O_{80})N_{30}P_2S$. Waters with suitable forms of carbon, nitrogen, phosphorus, and sulfur will support microbial growth. The temperature range over which living organisms can grow is that in which liquid water can exist, ~0–100°C. Microbial life is possible over a range of 10 pH units or more. Many microorganisms can withstand hundred-fold or greater variations in pressure. Heavy metal concentrations as low as $10^{-8}M$ can inhibit growth of some microorganisms, while others may be resistant to concentrations of a million-fold greater. Microbial species show thousand-fold differences in susceptibility to ultraviolet, β, and γ irradiation.

3. Biofilm Formation

It is convenient to discuss the characteristics of individual groups of microorganisms, however, in a natural environment, microorganisms form synergistic communities. These communities consist of biofilms that conduct combined processes that individual species cannot. The term biofilm describes a range of microbial associations (12). In aquatic environments, microbial cells attach to solids, including metals. Immobilized cells grow, reproduce, and produce extracellular polymers forming a biofilm (Fig. 2). Microorganisms colonize surfaces of all engineering materials, but there is a stochastic nature to a real coverage and

thickness that has never been successfully modeled. Bacteria in pure cultures or in consortia do not form uniform, predictable biofilms. Growth rate depends on substratum, available nutrients, temperature, and electron acceptors. Biofilm composition is affected by small perturbations in the environment, eg, temperature, nutrient concentration, and flow. The response of microorganisms within biofilms cannot be predicted with certainty. Clumps of cells can slough from surfaces transforming homogeneous biofilms to patchy ones.

Lewandowski (13) hypothesized that biofilm development optimizes survival of biofilm constituents and maximizes transport of nutrients into biofilms. Biofilms also provide protective environments for bacteria and in most cases allow different types of bacteria to flourish within different strata of the biofilm (14). For example, obligate anaerobic bacteria are routinely isolated from oxygenated environments in association with other bacteria that effectively remove oxygen from the immediate vicinity of the anaerobe. Bacteria within biofilms act symbiotically to produce conditions more favorable for the growth of each species. In an aerobic environment, bacteria near the fluid phase are provided with complex nutrients and oxygen. These bacteria use oxygen, break down carbon sources, and produce simple polymers and fatty acids. Bacteria within biofilms, use waste products generated by other bacteria as nutrients that are metabolized to fatty acids, carbon dioxide and hydrogen, acetate and hydrogen. It is extremely difficult to predict the impact of biofilms on degradation processes, including corrosion. Microorganisms within biofilms are capable of maintaining environments at biofilm–surface interfaces that are radically different from the bulk media in terms of pH, dissolved oxygen, and other organic and inorganic species. In some cases, these interfacial conditions could not be maintained in the bulk medium at room temperature near atmospheric pressure. Consequently, microorganisms within biofilms produce reactions that are not predicted by thermodynamic arguments based on the chemistry of the bulk medium.

4. Causative Organisms and Possible Mechanisms

Several mechanisms for MIC are related to the presence and activities of generic microorganisms in biofilms and not to specific microorganisms, eg, ennoblement, concentration cells, inactivation of corrosion inhibitors, and alteration of anion ratios.

4.1. Ennoblement. Biofilm formation on passive metals can shift the open-circuit potential (E_{corr}) in the noble direction, ie, ennoblement (Fig. 3), and produce accompanying increases in current density (15–17). For a concise review see Little and co-workers (18). Ennoblement of E_{corr} has been reported in fresh, brackish, and seawaters around the world. The alloys tested include, but are not limited to the following: UNS S30400, S30403, S31600, S31603, S31703, S31803, N08904, N08367, S44660, S20910, S44735, N10276, N06625, platinum, gold, palladium, chromium, titanium, and nickel. Attempts have been made to relate ennoblement to rate of localized corrosion, galvanic corrosion, crevice corrosion, initiation time of crevice corrosion and critical pitting potentials. Theoretically, E_{corr} ennoblement should increase the probability for pitting and crevice corrosion initiation and propagation of passive alloys for

which the pitting potential is within several hundred millivolts of E_{corr} (Fig. 4) (19). Numerous researchers have shown that increased cathodic reduction rates accompany ennoblement of E_{corr}. However, attempts to relate ennoblement to increased localized corrosion have been inconsistent. Comparison of ennoblement data among investigators is complicated because extent of ennoblement is affected by sample size, flow rate, temperature, and sample configuration. Martin and co-workers (20) compared ennoblement of several Ni–Cr–Mo alloys (N06625, N10276, N06059, N064555, N06686) and SS30400 at two coastal seawater locations: Key West, Florida, and Delaware Bay. The two exposure sites have different temperatures and different salinities. The authors demonstrated that extent of ennoblement varied between the two locations and that the extent of ennoblement for a particular material could not be used to predict an increased likelihood of localized corrosion for a crevice corrosion prone alloy, ie, 304 stainless steel.

In fresh and brackish water, ennoblement results from microbial surface deposition of manganese and localized corrosion of 300 series stainless steels has been related directly to the biomineralized deposits on the surface. Ennoblement in marine waters has been attributed to depolarization of the oxygen reduction reaction due to organometallic catalysis, microbial enzymes, unidentified extracellular chemicals, acidification of the electrode surface, combined effects of elevated hydrogen peroxide (H_2O_2) and decreased pH, and production of passivating siderophores.

4.2. Concentration Cells *Oxygen Concentration Cells.* Respiring aerobic microbial cells on metal surfaces can result in local anodes and cathodes and formation of differential aeration cells. Under aerobic conditions, areas under respiring colonies become anodic and surrounding areas become cathodic.

Metal Concentration Cells. Microorganisms that colonize metal surfaces produce extracellular polymeric substances (EPS) and form a gel matrix on the metal. In general, EPS are acidic and contain functional groups that bind metals (21). Metal ions concentrated from the aqueous phase or from the substratum into the biofilm can increase corrosion rates by providing an additional cathodic reaction (22–24).

4.3. Inactivation of Corrosion Inhibitor. Biofilms reduce the effectiveness of corrosion inhibitors by creating a diffusion barrier between the metal surface and the inhibitor in the bulk medium (25). Aliphatic amines and nitrites used as corrosion inhibitors can be degraded by microorganisms, decreasing the effectiveness of the compounds and increasing the microbial populations (26–28). Cooke and co-workers (29) reported that potassium chromate (K_2CrO_4) was ineffective as a corrosion inhibitor in an electricity generating station because of chromate reducing bacteria. The bacteria were causing blockage of pipes by precipitation of chromium(III) oxide.

4.4. Alteration of Anion Ratios. Microorganisms can alter the composition of an electrolyte and make it more corrosive. For example, molar ratios of aggressive ions to inhibiting ions (eg, Cl^- to $NO^{3-} + SO_4^{-2}$) are used to predict whether an electrolyte can sustain a localized corrosion reaction. Relationships between concentration of inhibitive and aggressive anions correspond to competitive uptake of the anions by adsorption or ion exchange at a fixed number of surface sites. Increasing chloride concentration shifts the critical pitting

potential to more active (negative) values. The potential is shifted to more noble (positive) values by the presence of other anions, particularly oxyanions (ClO_4^-, SO_4^{2-}, NO_3^-, PO_4^{3-}, NO_2^-, and OH^-). Salvarezza and co-workers (30) demonstrated that during growth of the fungus *Cladosporium resinae*, nitrate, and phosphate were incorporated into the biomass increasing the chloride/inhibitor ratio. In their experiments, fungal uptake of oxyanions was the principal cause of the pitting potential decrease during microbial growth. Predictions about pitting or crevice corrosion resistance in chloride-containing media cannot be based on anion ratios without consideration of potential microbial alterations (31).

4.5. Reactions Within Biofilms. Reactions within biofilms are generally localized, affecting mechanisms and accelerating rates of electrochemical reactions leading to corrosion. While corrosion influencing reactions may be attributed to a single group of organisms, the most aggressive MIC occurs with natural populations containing many types of microorganisms. Furthermore, a single type of microorganism can simultaneously affect corrosion via several mechanisms.

Methahogenesis. All known methanogens are both archaeans and obligate anaerobes. The role of archea in MIC is just beginning to be explored. Dinh and co-workers (32) suggest that an archaeon methaongen could obtain electrons directly from metallic iron. Similarly, Belay and Daniels (33) demonstrated that archae can use iron, aluminum, zinc, and cobalt as electron donors in methanogenesis.

Respiration–Photosynthesis. Algae and photosynthetic bacteria use light to produce oxygen that can accumulate within biofilms. Increased oxygen concentration can depolarize the cathodic reaction, leading to increased corrosion rates. During dark periods algae respire, converting oxygen to CO_2. Localized respiration–photosynthesis can lead to differential aeration cells and localized anodes and cathodes.

Sulfide Production. Reduction of elemental sulfur or thiosulfate ($S_2O_3^{2-}$) (34) results in production of hydrogen sulfide ion (HS^-), which is stable at neutral pH values. At more acidic pH values, HS^- converts to hydrogen sulfide (H_2S). Sulfide (S^{2-}) is only formed in highly basic (pH > 12) conditions. In the field of MIC, "sulfide" is used as a general descriptor of reduced sulfur species whether as an ionic species (eg, HS^-) or as a metal sulfide (eg, FeS).

Sulfate-reducing bacteria (SRB) are the organisms most closely identified with MIC. These bacteria are a group of ubiquitous, diverse anaerobes that use sulfate as the terminal electron acceptor, producing HS^-. They have been isolated from a variety of environments (35,36), including seawater where the concentration of sulfate is typically 25 m*M* (36). Even though the oxygen content of seawater above the thermocline ranges from 5–8 ppm, anaerobic microorganisms survive in anaerobic microniches until conditions are suitable for their growth (37,38). If the aerobic respiration rate within a biofilm is greater than the oxygen diffusion rate, the metal–biofilm interface can become anaerobic and provide a niche for sulfide production by SRB (39). The critical biofilm thickness required to produce anaerobic conditions depends on availability of oxygen and the respiration rates of organisms in the biofilm. The metabolic activity of SRB cause accumulation of sulfide near metal surfaces. Sulfate-reducing bacteria have been the focus of many investigations involving MIC and several

corrosion mechanisms have been attributed to SRB, including cathodic depolarization by the enzyme dehydrogenase, anodic depolarization, release of exopolymers capable of binding metal ions, sulfide induced stress corrosion cracking, hydrogen induced cracking or blistering, and production of metal sulfides. Recent reviews suggest that SRB can influence a number of corrosion mechanisms simultaneously.

McNeil and Odom (40) developed a thermodynamic model for predicting the likelihood that a metal would react with microbiologically produced sulfide. The model is based on the assumption that SRB MIC is initiated by sulfide-rich reducing conditions in the biofilm and that under those conditions, the oxide layer on the meal (or the metal itself) is destabilized and acts as a source of metal ions. The metal ions react to produce sulfide compounds. If the reaction to convert the metal oxide to a metal sulfide has a positive Gibbs free energy under surface conditions, the sulfides will not strip the protective oxide and no corrosion will take place. If the Gibbs free energy for that reaction is negative, the reaction and corrosion will proceed. The model accurately predicts that carbon steel and copper alloys will be susceptible and that titanium and stainless steels containing 6% or more molybdenum will be immune to reactions with sulfide. The model is limited to thermodynamic predictions as to whether or not a reaction will take place and does not consider metal toxicity to the organisms, tenacity of the resulting sulfide, or other factors that influence reaction kinetics and corrosion rates.

Acid Production. Elemental sulfur, thiosulfates, metal sulfides, H_2S, and tetrathionates can be oxidized to sulfuric acid by microorganisms generically referred to as thiobacilli or sulfur oxidizing bacteria (SOB). Heterotrophic bacteria that secrete organic acids during fermentation of organic substrates are referred to as acid producing bacteria (APB). The kinds and amounts of acids produced depend on the type of microorganisms and the available substrate molecules. Organic acids may force a shift in the tendency for corrosion to occur. Organic acids produced by fungi were identified as the cause for pitting failures in painted carbon steel holds of a bulk carrier (41) and aluminum fuel storage tanks (30).

Ammonia Production. Many organisms including nitrate-reducing bacteria can produce ammonia (NH_3) from the metabolism of amino acids or the reduction of nitrite- or nitrate-forming ammonium (NH_4^+). Nitrate-based corrosion inhibitors can be a source of nitrogen for microbial ammonia production. Pope (27) and Pope and co-workers (28,29) discussed potential corrosion in copper alloys, particularly stress corrosion cracking, due to the activities of ammonia-producing bacteria.

Metal Oxidation/Deposition. Biomineralization of iron and manganese oxides occurs widely in natural waters and can be carried out by a variety of organisms including bacteria, yeast, and fungi (42). Ghiorse (43) prepared a review of metal-depositing microorganisms in which he identified microorganisms that catalyze the oxidation of metals, others that accumulate abiotically oxidized metal precipitates, and still others that derive energy by oxidizing metals.

Manganese. Manganese oxidation is coupled to cell growth and metabolism of heterotrophic substrates (44–46). While Mn^{2+} (manganous) is soluble, all the various manganic oxidized forms (valence state > +2), Mn_3O_4, Mn_2O_3,

MnOOH, MnO_2, are insoluble. Microbially deposited manganese oxide on a stainless steel in freshwater caused an increase in E_{corr} and increased cathodic current density (47). Given sufficient conductivity in the tubercle, much of this material may serve as a cathode to support corrosion at the oxygen-depleted anode within the tubercle. Continued biomineralization within a large tubercle may sustain a significant amount of the cathodic current. Both factors can increase the risk of stainless steel corrosion. The extent to which the elevated current density can be maintained is controlled by the electrical capacity of the mineral reflecting both total accumulation and conductivity of the mineral-biopolymer assemblage (only material in electrical contact with the metal will be cathodically active). The biomineralization rate and the corrosion current control oxide accumulation, where high corrosion currents will discharge the oxide as rapidly as it is formed. This variation in accumulation causes the oxides to exert different modes of influence on the corrosion behavior of active metals compared with passive metals.

Iron. Iron-oxidizing bacteria (FeOB) have been implicated in microbiologically influenced corrosion since the 1960s (48). Iron-oxidizing bacteria derive energy from the oxidation of ferrous (Fe^{2+}) to ferric (Fe^{3+}) at/near neutral pH and in some cases the result is the formation of dense tubercles or rusticles of filamentous iron oxides. Most FeOB are microaerophilic and those that have received the most attention in MIC are *Gallionella, Sphaerotilus, Leptothrix, Siderocapsa*, and *Crenothrix*. The presence of dense tubercles and fragile rusticles are often used to diagnose FeOB MIC. In a few instances, the twisted iron-encrusted *Gallionella* stalks or *Leptothrix* sheaths have been imaged with light or scanning electron microscopy (SEM). The environments, substrata, and FeOB found in tubercles and rusticles are listed in Table 1 (49).

Tubercle formation attributed to FeOB has been documented in untreated well water and chlorinated drinking water on carbon and stainless steels (Fig. 5a–c). Most of the documented case histories of MIC associated with FeOB tubercle formation have involved exposure of a 304 or 316 stainless steel and the corrosion mechanism is under-deposit corrosion or formation of a differential aeration cell (5,50,51). Under stagnant conditions, FeOB form dense deposits within months, excluding oxygen from the area immediately under the deposit and initiating a series of events that are individually or collectively very corrosive. In an oxygenated environment, the area deprived of oxygen becomes a relatively small anode compared to the large surrounding oxygenated cathode. At the anode, metal is oxidized and pH decreases. The extent of the decrease is determined by the alloy composition (52). For this reason, underdeposit attack is particularly aggressive on 300 series stainless steels, which contain a minimum of 16.0% chromium. In addition, chlorides from the electrolyte migrate to the anode to neutralize any buildup of charge, forming heavy metal chlorides that are extremely corrosive. Under these circumstances, pitting involves the conventional features of differential aeration, a large cathode: anode surface area, and the development of acidity and metallic chlorides.

Rusticles can form in salinities ranging from freshwater to seawater (35 0/00) at varying temperatures and depths. There have been no explanations of the specific conditions that result in the formation of tubercles versus rusticles. The term "rusticle" was coined by Ballard (53) to describe rust features covering

the wreck of the ocean liner RMS *Titanic* (Fig. 6a–b). The wreck has been at a depth of 3800 m for 95 years at a temperature of 1°C and 6000 psi. He described these features as very fragile reddish brown stalactites of rust hanging down as much as several feet, caused by "iron-eating bacteria" (53). Cullimore and Johnson (54,55) described rusticles on the *Titanic* as, "a complex of microbial communities within an iron-rich and calcium deficient porous-like home". They proposed a corrosion mechanism whereby FeOB "were extracting iron from the steel of the ship and then exporting that iron into the oceanic environment as red dust and yellow colloids". They further observed more rusticle-type growth in 1998 than in 1996. Stoffyn-Egli and Buckley (56,57) studied the mineralogy and microbiology of rusticles recovered from the *Titanic* and concluded that bacteria caused the precipitation of an outer shell of lepidocrocite (γ-FeOOH) and that the interior of the rusticle was euhedral goethite (α-FeOOH) crystals. In addition to FeOB, they identified SRB as responsible for rusticle formation. They proposed a theoretical mechanism for rusticle formation that included SRB, reducing conditions on a small scale within rust flakes, and the coexistence of minerals with different redox potentials. Long (58) used Mossbauer spectroscopy to identify small particles of goethite, traces of quartz and green rust in rusticles from the *Titanic*. Herdendorf and co-workers (59) described similar formations on the wreck of the SS *Central America*, a wooden steamer with iron machinery that has been on the floor of the North Atlantic Ocean in 2200-m water for 144 years (5.6-mg/L O_2). *Leptrothrix* and *Siderocapsa* were tentatively identified as the organisms causing the rusticles. Rusticles have been identified on the iron surfaces of the USS *Monitor*, an ironclad warship (60,61). The outer casing is siderite ($FeCO_3$), lepidocrocite, and goethite. The inner core has a pH 3 and contains unstable magnetite. The organism associated with rusticles on the *Monitor* is *Gallionella*. Rusticles have been reported on shipwrecks in depths of 30–60 m in Lake Superior, eg, *Comet*, *Osborne*, and *Edmund Fitzgerald*. Rusticles have been used to inoculate media and demonstrate accelerated corrosion.

Metal Reduction. Dissimilatory iron and/or manganese reduction occurs in several anaeobic and facultative microorganisms, collectively called metal-reducing bacteria (MRB). Inhibitor and competition experiments suggest that Mn^{4+} and Fe^{3+} are efficient electron acceptors (Fig. 7) (62) similar to nitrate in redox ability and are capable of out-competing electron acceptors of lower potential, such as sulfate or carbon dioxide (63).

5. Diagnosing MIC

Diagnosing MIC after it has occurred requires a combination of microbiological, metallurgical, and chemical analyses. The objective is to have independent measurements that are consistent with a mechanism for MIC. The following are required for an accurate diagnosis of MIC: (*1*) a sample of the corrosion product or affected surface that has not been altered by collection or storage, (*2*) identification of a corrosion mechanism, (*3*) identification of microorganisms capable of growth and maintenance of the corrosion mechanism in the particular environment, and (*4*) demonstration of an association of the microorganisms with the observed corrosion. The MIC investigations have typically attempted

to (*1*) identify causative microorganisms in the bulk medium or associated with the corrosion products, (*2*) identify a pit morphology consistent with an MIC mechanism, and (*3*) identify a corrosion product chemistry that is consistent with the causative organisms. It is essential in diagnosing MIC to demonstrate a spatial relationship between the causative microorganisms and the corrosion phenomena. For many years, the first step in identifying corrosion as MIC was to determine the presence of specific groups of bacteria in the bulk medium (planktonic cells) or associated with corrosion products (sessile cells). There are four approaches: (*1*) culture the organisms on solid or in liquid media, (*2*) extract and quantify a particular cell constituent, (*3*) demonstrate–measure some cellular activity, or (*4*) demonstrate a spatial relationship between microbial cells and corrosion products using microscopy.

5.1. Identification of Causative Organisms. Classifying the archaea is still difficult, since the vast majority of these organisms have never been studied in the laboratory and only have been detected by analysis of their nucleic acids in samples from the environment.

The method most often used for detecting and enumerating groups of bacteria is the serial dilution-to-extinction method using selective culture media. To culture microorganisms, a small amount of liquid or a suspension of a solid (the inoculum) is added to a solution or solid that contains nutrients (culture medium). There are three considerations when growing microorganisms: type of culture medium, incubation temperature, and length of incubation. The present trend in culture techniques is to attempt to culture several physiological groups including aerobic, heterotrophic bacteria; facultative anaerobic bacteria; SRB and APB. Growth is detected as turbidity or a chemical reaction within the culture medium. Traditional SRB media contain sodium lactate as the carbon source (36,64). When SRB are present in the sample, sulfate is reduced to sulfide, which reacts with iron (either in solution or solid) to produce black ferrous sulfide. Culture media are typically observed over several days (30 days may be required for growth of SRB). The distinct advantage of culturing techniques to detect specific microorganisms is that low numbers of cells grow to easily detectable higher numbers in the proper culture medium. However, there are numerous limitations for detection and enumeration of cells by culturing techniques. Changes in microflora occur as a result of water storage. Under all circumstances, culture techniques underestimate the organisms in a natural population (65,67). Another major problem in assessing microorganisms in natural environments is that viable microorganisms can enter into a nonculturable state (68). Culture media cannot approximate the complexity of a natural environment. Growth media tend to be strain-specific. For example, lactate-based media sustain the growth of lactate oxidizers, but not acetate-oxidizing bacteria. Incubating at one temperature is further selective. The type of medium used to culture microorganisms determines to a large extent the numbers and types of microorganisms that grow. Zhu and co-workers (69) demonstrated dramatic changes in the microbial population from a gas pipeline after samples were introduced into liquid culture media. For example, using culture techniques SRB dominated the microflora in most pipeline samples. However, by using culture-independent genetic techniques, they found that methanogens were more abundant in most pipeline samples than denitrifying bacteria and that SRB were the least

abundant bacteria. Similarly, Romero and co-workers (70) used genetic monitoring to identify bacterial populations in a seawater injection system. They found that some bacteria present in small amounts in the original waters were enriched in the culture process.

Genetic techniques using ribosomal rubonucleic acid (rRNA) or rDNA have been used to identify and quantify microbial populations in natural environments (71–73). Comparison of the data demonstrates that culture-dependent approaches underestimate the complexity of microbial communities. Zhu and co-workers (74,75) used genetic techniques to characterize the types and abundance of bacterial species in gas pipeline samples and made similar observations. Another example of genetic techniques is the fluorescent *in situ* hybridization (FISH), which uses specific fluorescent dye-labeled oligonucleotide probes to selectively identify and visualize bacteria (71).

Biochemical assays measure constitutive properties including adenosine triphosphate (ATP) (76), phospholipid fatty acids (PLFA) (77), cell-bound antibodies (78), adenosine-5′-phosphosulfate (APS) reductases (79), and hydrogenase (80). Unlike culturing techniques, biochemical assays for detecting and quantifying bacteria do not require growth of the bacteria.

Roszak and Colwell (68) reviewed techniques commonly used to detect microbial activities in natural environments, including transformations of radiolabeled metabolic precursors. Phelps and co-workers (81) used a variety of ^{14}C-labeled compounds to quantify bacterial activities associated with corrosion tubercles in steel natural gas transmission pipelines. They demonstrated that organic acid was produced from hydrogen and carbon dioxide in natural gas by acetogenic bacteria, and that acidification could lead to enhanced corrosion of the steel. Maxwell (82) developed a radiorespirometric technique for measuring SRB activity on metal surfaces that involved two distinct steps: incubation of the sample with ^{35}S sulfate and trapping the released sulfide.

Light microscopy, epifluorescence microscopy, confocal laser scanning microscopy, atomic force microscopy, scanning, and transmission electron microscopy have been used to image the relationship between microorganisms and corrosion products (9). There are fundamental problems in attempting to diagnose MIC by establishing a spatial relationship between numbers and types of microorganisms in the bulk medium or those associated with corrosion products using any of the techniques previously described.

Zintel and co-workers (83) established that there were no relationships between the presence, type or levels of planktonic, or sessile bacteria and the occurrence of pits. Because microorganisms are ubiquitous, the presence of bacteria or other microorganisms does not necessarily indicate a causal relationship with corrosion. In fact, microorganisms can nearly always be cultured from natural environments. Little and co-workers (84) reported that electrochemical polarization could influence the number and types of bacteria associated with the surface. de Sanchez and Schiffrin (85) demonstrated that Cu^{2+} and titanium ions were strong attractants for *Pseudomonas* sp. Detection or demonstration of bacteria associated with corrosion products or corrosion sites is not an independent diagnostic for MIC.

5.2. Pit Morphology. Pope (86) completed a study of gas pipelines to determine the relationship between extent of MIC and the levels–activities

of SRB. He concluded that there was no relationship. Instead he found large numbers of APB and organic acids, particularly lactic acid, and identified the following metallurgical features in carbon steel: large craters from 5 to 8 cm or greater in diameter surrounded by uncorroded metal; cup-type hemispherical pits on the pipe surface or in the craters; striations or contour lines in the pits or craters running parallel to longitudinal pipe axis (rolling direction); and tunnels at the ends of the craters also running parallel to the longitudinal axis of the pipe.

Pope (86) reported that these metallurgical features were "fairly definitive for MIC". However, the author did not advocate diagnosis of MIC based solely on pit morphology. Subsequent research has demonstrated that these features can be produced by abiotic reactions (87) and cannot be used to independently diagnose MIC.

Other investigators described ink bottle shaped pits in 300 series stainless steel that were supposed to be diagnostic of MIC. Borenstein and Lindsay (50,51) reported that dendritic corrosion attack at welds was "characteristic of MIC". Chung and Thomas (88) compared MIC pit morphology with non-MIC chloride-induced pitting in 304/304L and 308 stainless steel base metals and welds. They concluded that there were no unique morphological characteristics for MIC pits in these materials. The problem that has resulted from the assumption that pits can be independently interpreted as MIC is that MIC is often misdiagnosed. For example, Welz and Tverberg (89) reported leaks at welds in a stainless steel (316L UNSS31603) hot water system in a brewery after 6 weeks in operation were due to MIC. The original diagnosis was based on the circumstantial evidence of attack at welds and the pitting morphology of scalloped pits within pits. However, after a thorough investigation MIC was dismissed. There were no bacteria associated with the corrosion sites and deposits were too uniform to have been produced by bacteria. The hemispherical pits had been produced when CO_2 was liberated and low pH bubbles nucleated at surface discontinuities.

5.3. Chemical Testing. Analyses for corrosion product chemistry can range from simple field tests to mineralogy and isotope fractionation. Field tests for solids and corrosion products typically include pH and a qualitative analysis for the presence of sulfides and carbonates. Elements in corrosion deposits can provide information as to the cause of corrosion. Energy dispersive X-ray analysis (EDS) coupled with SEM can be used to determine the elemental composition of corrosion deposits. Because all living organisms contain ATP, a phosphorus peak in an EDS spectrum can be related to microbial cells associated with the corrosion products. Other sources of phosphorus, eg, phosphate water treatments, must be eliminated. The activities of SRB and manganese oxidizing bacteria produce surface bound sulfur and manganese, respectively. Chloride is typically found in crevices and pits and cannot be directly related to MIC.

There are several limitations for EDS surface chemical analyses. Samples for EDS cannot be evaluated after heavy metal coating, so that EDS spectra must be collected prior to heavy metal coating. It is difficult or impossible to match spectra with exact locations on images. This problem is not a problem with the environmental scanning electron microscopy (ESEM)

because nonconducting samples can be imaged directly, meaning that EDS spectra can be collected from area that is being imaged by ESEM. Little and co-workers (90) documented the changes in surface chemistry as a result of solvent extraction of water, a requirement for SEM. Other shortcomings of SEM–EDS include peak overlap. Peaks for sulfur overlap peaks for molybdenum and the characteristic peak for manganese coincides with the secondary peak for chromium. Wavelength dispersive spectroscopy can be used to resolve overlapping EDS peaks. Peak heights cannot be used to determine the concentration of elements. It is also impossible to determine the form of an element with EDS. For example, a high sulfur peak may indicate sulfide, sulfate, or other forms of sulfur.

Bacteria do produce corrosion products that could not be produced abiotically in near surface environments, resulting in isotope fractionation and mineralogical fingerprints. McNeil and co-workers (91) used mineralogical data determined by X-ray crystallography, thermodynamic stability diagrams (Pourbaix), and the simplexity principle for precipitation reactions to evaluate corrosion product mineralogy. They concluded that many sulfides formed under near surface natural environmental conditions could only be produced by microbiological action on specific precursor metals. They reported that djurleite ($Cu_{31}S_{16}$), spinonkopite ($Cu_{1.4}S$), and the high temperature polymorph of chalcocite (Cu_2S) were mineralogical fingerprints for SRB induced corrosion of copper–nickel alloys. They also reported that the stability or tenacity of sulfide corrosion products determined their influence on corrosion.

The stable isotopes of sulfur (^{32}S and ^{34}S), naturally present in any sulfate source, are selectively metabolized during sulfate reduction by SRB and the resulting sulfide is enriched in ^{32}S (92) The ^{34}S accumulates in the starting sulfate as the ^{32}S is removed and becomes concentrated in the sulfide. Little and co-workers (93) demonstrated sulfur isotope fractionation in sulfide corrosion deposits resulting from activities of SRB within biofilms on copper surfaces. The isotope ^{32}S accumulated in sulfide-rich corrosion products, ^{34}S was concentrated in the residual sulfate in the culture medium. Accumulation of the lighter isotope was related to surface derivatization or corrosion as measured by weight loss. Use of this technique to identify SRB-related corrosion requires sophisticated laboratory procedures.

6. Measuring and Monitoring MIC

Electrochemical techniques used to study MIC include those in which no external signal is applied [eg, measurement of galvanic current with zero resistance ammeter (ZRA), measurement of redox potential ($E_{r/o}$), corrosion potential (E_{corr}) and electrochemical noise analysis (ENA)], those in which only a small potential or current perturbation is applied [eg, polarization resistance (R_p), and electrochemical impedance spectroscopy (EIS)], and those in which the potential is scanned over a wide range (eg, anodic and cathodic polarization curves, pitting scans) (94).

Biofilm formation and corrosion can be monitored using metal coupons implanted either in-line or in a side stream. Several types of coupon holders

have been developed. Typically, coupons are removed periodically and used for weight loss, microbiological analyses, or microscopic examination.

Many techniques claim to monitor MIC, however, none have been accepted as an industry standard or as a recommended practice by ASTM or NACE International. The major limitation for MIC monitoring programs is the inability to relate microbiology to corrosion in real time. Some techniques can detect a specific modification in the system due to the presence and activities of microorganisms (eg, heat transfer resistance, fluid friction resistance, galvanic current) and assume something about the corrosion. Others measure some electrochemical parameter (eg, R_p, ENA) and assume something about the microbiology. With experience and knowledge of a particular operating system either technique type can be an effective monitoring tool, especially for evaluating a treatment regime (biocides or corrosion inhibitors).

All monitoring techniques used for MIC are based on assumptions that can only be validated by a thorough understanding of the system that one is attempting to monitor. Planktonic population does not properly reflect the type and number of organisms living in the biofilm. Polarization resistance is appropriate for indicating a change in the general corrosion rate, but the results are difficult to interpret for localized corrosion. Measurements of R_p will indicate that something is happening, but will not give an accurate measure of the localized corrosion rate. Impedance spectroscopy requires the area of attack to be determined in order to calculate the corrosion rate. When MIC is present, corrosion is usually highly non-uniform. Thus, knowing the electrode sample surface area used in the measurement is often not sufficient. The ENA techniques have failed to routinely predict MIC events accurately under field conditions and ZRA measurements of galvanic current cannot be directly converted to corrosion rate.

7. Impact of Engineering Practices on Susceptibility to MIC

7.1. Welding. In general, procedures (eg, welding and alloying) and design practices that make materials more or less vulnerable to other types of corrosion have the same impact on MIC. Welding, a nonequilibrium process, produces nonequilibrium microstructure, altering the size, shape, amount, composition, and distribution of microstructural constituents in the fusion zone and the heat affected zone (HAZ). Preferential corrosive attack at weld-modified regions has been demonstrated for 304L, 316L (Fig. 8**a**,**b**) (95), AL6XN, alloy 400, and Al5086. Welding may influence MIC by changing the following: surface texture, solute distribution, phase boundaries, grain size effects, localized melting, precipitates and inclusions, surface oxidation, and residual stress (96).

7.2. Hydrotesting. Many case histories of MIC are directly related to stagnant, microbiologically active waters. In abiological corrosion, stagnant waters tend to become less corrosive with time as aggressive ions (eg, chloride or sulfide) react. In biologically active environments, microorganisms produce deposits, acids, or sulfides. Their growth can continue as long as conditions are conducive for growth, making conditions more corrosive over time. As a result of widely publicized failures due to poor hydrotest waters and practices, Kobrin (97)

developed a list of prioritized preferred hydrotest waters and practices for the chemical process industries:

1. Use demineralized water, drain and dry as soon as possible after hydrotesting. (MIC has been reported in systems maintained with stagnant demineralized water.)
2. Use high purity steam condensate with early draining and drying.
3. Use natural, fresh water (river, pond, canal, well, etc), drain immediately, flush with demineralized water or steam condensate, blow or mop dry within 3–5 days.

Stagnant storm water, rain water, or melted snow are environments for microbial growth. Many operating systems require stagnant water and cannot be drained or dried. For example, some fire protection systems remain charged with water for long periods of time.

7.3. Alloying Elements *Low Alloy Steels.* Alloying elements alter the formation, chemical composition, thickness and tenacity of corrosion products, and may increase or decrease susceptibility to MIC. Walsh and co-workers (98) demonstrated extensive subgrain boundaries coupled with solute redistribution in the fusion zone as a result of welding and MIC. These results suggested that welding created a continuous network of sulfur-rich compounds that increased the sensitivity of carbon steel (wt%: C, 0.32; Cr, 0.50; Mn, 0.80, Mo, 0.02; Ni, 0.55; Fe, bal.) to MIC. Willis and Walsh (99) evaluated the effect of minor element content (wt%: Si, 0.13–0.49; S, 0.003–0.023; Ce, 0.010–0.015) on the susceptibility of low alloy steels to MIC in anaerobic aqueous systems. They found that sulfide inclusion sites were strongly correlated with increased MIC susceptibility. Pit initiation and propagation occurred most often at sulfide inclusions. For exposures > 4 h, microbial congregation and proliferation were markedly affected by inclusion size, shape, and composition. Sulfur content was directly correlated with the initiation of pits at inclusion sites and directly related to the number of tubercles that developed a much greater surface roughness. Larger, elongated inclusions increased the probability of pit initiation. Addition of Ce decreased sulfide inclusion length and aspect ratios regardless of other compositional variables. Pit initiation, pit depth, and pit volume decreased when Ce was added to carbon steel.

Copper and Nickel Alloys. Blue water (also called copper by-product release or cuprosolvency) (100) has been observed in copper tubing, primarily in soft potable waters after a stagnation period of several hours to days and is typically associated with copper concentrations of 2–20 mg/L (101). Blue water has been reported in New Zealand, Australia, the United States, Japan, and Europe (102). In all cases, the potable water was a soft, weakly buffered and slightly alkaline water prepared from a surface water (103). Both the cold and hot water systems were affected. This phenomenon is distinct from other types of copper corrosion in that it does not significantly compromise the integrity of the tube, but instead leads to copper contamination and coloring of the water. Webster and co-workers (102) concluded that biofilms were important in creating and maintaining a low interfacial pH. Decreased pH and incorporation of bacterially produced EPS into the copper oxide film, decreased the protective nature of the oxide and created the conditions for blue water.

Copper–nickel alloys containing < 35% nickel behave like copper. Differential aeration cells and microbial products including CO_2, H_2S, NH_3, organic, and inorganic acids are reported mechanisms for MIC of copper alloys.

The formation of a protective film on nickel is aided by the presence of iron, aluminum, and silicon. In high velocity seawater, nickel alloys are superior to predominantly copper alloys because the protective surface film remains intact under highly turbulent and erosive conditions.

Nickel–copper alloys (Table 2) (104) are susceptible to MIC. For example, alloy 400 is susceptible to pitting and crevice corrosion attack where chlorides penetrate the passive film. Sulfides can cause either a modification or breakdown of the oxide layer. Schumacher (105) reported that Monel 400 was susceptible to underdeposit corrosion and oxygen concentration cells formed by bacteria. Gouda and co-workers (106), Little and co-workers (107), and Pope (108) demonstrated pitting of alloy 400 tubes under deposits of bacteria. Nickel was selectively dealloyed.

No evidence for MIC in nickel–chromium and nickel–chromium–molybdenum alloys (Table 2) has been reported. Enos and Taylor (107) demonstrated that SRB did not cause corrosion of welded alloy 625. Martin and co-workers (110) evaluated Alloy 22, a candidate packaging material for nuclear waste containment was evaluated in simulated, saturated repository environment consisting of crushed rock from the repository site and a continual flow of simulated ground water for periods up to 5 years. They were able to demonstrate micron scale surface alterations due to the presence and activities of microorganisms.

Stainless Steels. Kovach and Redmond (111) suggested positive correlations between the ferric chloride test and service experience of stainless steels, meaning that resistance to MIC could be predicted from alloy composition. Table 3 (102) lists the chemical compositions of select stainless steels. Accordingly, their hypothesis predicts that resistance to MIC would increase with increased concentrations of chromium and molybdenum in an alloy. For example there are numerous reports of MIC in 304 and 316. Scott and Davies (112) reported failure of 904L heat exchanger after exposure to stagnant brackish and seawater that had been excessively chlorinated. However, there are no known instances of MIC during actual service of 6% molybdenum stainless, in spite of the fact that these steels have been used extensively in service water and other waters known to produce MIC. One of the most common forms of MIC attack in austenitic stainless steel is pitting at or adjacent to welds at the heat affected zone, the fusion line, and in the base metal (97). Borenstein (113) made the following observations for MIC in 304L and 316L weldments: both austenite and delta ferrite phases may be susceptible; combinations of filler and base materials have failed, including matching, higher and lower alloyed filler combinations; and solution annealing and pickling may produce welds that are less susceptible. A lack of sensitization in austenitic welds did not ensure protection. Additionally, surface conditions commonly associated with corrosion resistance, such as heat tint, and those related to residual stresses, including gouges and scratches, may increase susceptibility. Kearns and Borenstein (114) state that welds having filler metal compositions matching the base metal have lower corrosion resistance than fully annealed base metal due to lack of homogeneity and the microsegregation of chromium and molybdenum. Chemically depleted

regions can be much more susceptible to localized attack. Stein (115) reported that MIC susceptibility of base metal related to weld area was not related to sensitization but to the microstructure produced during the manufacturing process. Reannealing reduced the severity of the pitting corrosion. Sreekumari and co-workers (116) evaluated bacterial attachment to stainless steel weldments and the significance of substratum microstructure. Their results demonstrated that bacteria colonized more weld coupons than base metal coupons. They further demonstrated that initial attachment occurred along the grain boundaries–austenite-ferrite interfaces, suggesting the influence of microstructure. The area of attachment was inversely proportional to the average grain size and bacterial colonization started on grain boundaries. Weld areas had more grains, more grain boundaries, and consequently more attached bacteria. Elemental segregation during welding and/or differential energy distribution between the matrix and the grain boundaries was suggested as the possible reason for the pattern of attachment. Amaya and co-workers (117) demonstrated that bacterial adhesion increased at the base of the weld and heat-affected zone of 304 stainless steel coupons with 308 filler in incubations with some stirring (reciprocal shaking). They attributed pitting at the base of the weld to increased bacterial adhesion and a defective passive film at that location.

Aluminum and Aluminum Alloys. The corrosion resistance of aluminum and its alloys is due to an aluminum oxide passive film. Anodizing produces thicker insulating films and better corrosion resistance. The natural film on aluminum alloys can be attacked locally by halide ions. The susceptibility of aluminum and its alloys to localized corrosion makes it particularly vulnerable to MIC. Most reports of MIC are for aluminum (99%), 2024, and 7075 alloys used in aircraft or in underground fuel storage tanks (118). Localized corrosion attributed to MIC occurs in the water phase of fuel–water mixtures in the bottom of tanks and at the fuel-water interface. Contaminants in fuel include surfactants, water, and water soluble salts that encourage growth of bacteria and fungi. Two mechanisms for MIC of aluminum alloys have been documented: production of water soluble organic acids by bacteria and fungi, and formation of differential aeration cells.

Titanium. There are no case histories of MIC for titanium and its alloys. Schutz (119) reviewed mechanisms for MIC and titanium's corrosion behavior under a broad range of conditions. He concluded that at temperatures $< 100°C$ titanium is not vulnerable to iron–sulfur-oxidizing bacteria, SRB, APB, differential aeration cells, chloride concentration cells, or hydrogen embrittlement.

Antimicrobial Metals. Sreekumari and co-workers (120) evaluated the antimicrobial properties and corrosion behavior of silver alloyed 304 type stainless steel and its welds (Table 4). In an effort to make stainless steel antimicrobial and thus enhance its resistance to MIC, two types of stainless steels were prepared - silver coated and silver alloyed. Bacterial adhesion to these materials was compared to adhesion on 304 stainless steel controls. The area of bacterial adhesion was found to be significantly less in the case of silver incorporated coupons compared to the controls. Silver alloyed coupons showed more antimicrobial effect then silver painted coupons. The SEM observations indicated that control coupons pitted within 30 days. Free corrosion potential showed ennoblement in the case of the control coupons. Silver coated coupons also showed an increase in

potential while silver alloyed coupons did not. These experiments were completed with *Pseudomonas* sp. in a dilute nutrient medium.

Nandakumar and co-workers (121) evaluated the antimicrobial properties of a magnesium alloy, AZ31B (wt%: Al, 3.0; Mn, 0.46; Zn, 1.0; Si, Cu, <0.01; Ni, 0.001; Fe, 0.005; Ca, <0.01; Mg, bal.) in laboratory experiments with *Pseudomonas* sp. They observed a high rate of bacterial attachment in days 1 and 2. However, by day 6, the coverage was reduced. The total viable numbers were also reduced. The authors determined that magnesium reacts with water to produce magnesium hydroxide, which forms a film on the metal surface. The formation of the film caused an elevation of surface pH into the alkaline region. The combined effect of high pH and concentration of Mg^{2+} adversely affected the growth and survival of *Pseudomonas* sp. both in the medium and on the surface. They concluded that over the 6-day period magnesium alloys exhibited antibacterial properties that prevented bacterial attachment and biofilm formation.

7.4. Polymeric Materials. Possible mechanisms for microbial degradation of polymeric materials include direct attack by acids or enzymes, blistering due to gas evolution, enhanced cracking due to calcareous deposits and gas evolution, and polymer destabilization by concentrated chlorides and sulfides. Polymeric materials are also subject to degradation from moisture intrusion and osmotic blistering. Both may be influenced by biofilms. Organic additives including plasticizers, fillers, and stabilizers, many of the ester type, may provide nutrients for microbial growth and ultimate degradation. van der Mei and co-workers (122) evaluated the biodeterioration of silicone rubber used for voice prosthesis. Gettleman and co-workers (123) reported that silicone rubber dental liners could be degraded by yeasts.

Moisture and chemical resistant polymeric coatings and linings are used to protect underlying metals against corrosion. Coating performance is influenced by composition, thickness, continuity, adhesion to the metal substratum, and resistance to microbial degradation. Microbial production of acids and enzymes may result in selective leaching of coating components with increased ion transport and porosity. Dittmer and co-workers (124) evaluated the corrosion of iron pipes, encapsulated by a polyethylene film, exposed to SRB. They reported that polyethylene was susceptible to microbial breakdown. The coatings were permeable to water and to soluble sulfide. With increasing time, the corrosion rate and weight losses of the coated specimens were similar to the uncoated specimens. Jack and co-workers (125) evaluated coatings in biologically active soils. They found that wet, clay-rich soils fostered higher populations of bacteria than moist sandy soils and that polyethylene tape supported higher counts of bacteria then extruded polyethylene or fusion-bonded epoxy coatings presumably due to the presence of degradable adhesive primer components in the tape. Gu and co-workers (126) studied fungal degradation of polyimide films used as insulators in electronic packaging. Kay and co-workers (127) demonstrated reduction in tensile strength and percentage elongation at break for polyester polyurethanes exposed to bacteria. Stranger-Johannessen (128) confirmed fungal degradation of polyurethane cable sheathing in the marine environment.

Gu and co-workers (129) reported fungal degradation of carbon-reinforced epoxy, carbon-reinforced bismaleimide, and glass-reinforced fluorinated

polyimide composites due to hyphae penetration into resin interiors. The authors concluded that microorganisms derived energy from resins and fiber sizings. Polyester polyurethanes and other polyesters are readily broken down by microbial esterases. The resistance of polyester polyurethanes depends on the type of diol. Low molecular weight, unbranched alkane diols tend to be susceptible.

7.5. Concrete. Concrete is an inert aggregate, such as rock and gravel, surrounded by a cement binder. Concrete is a moderately porous mixture of alkaline inorganic precipitates and mineral aggregates, primarily hydrated calcium silicate and portlandite, $Ca(OH)_2$. Microbiologically influenced corrosion in concrete sewers has been described by investigators around the world (130–134). Severyn (135) estimates that the deterioration of concrete in waste water collection and treatment systems is primarily due to biodegradation and that > $100 million are spent annually to replace manholes, wet wells, concrete pipes, treatment facilities and grit chambers. Kulpa and Baker (136) and Mansfeld and co-workers (137,138) describe the complex biodegradation process in sewage collection systems involving aerobic and anaerobic bacterial mediation of the sulfur cycle (Fig. 9). Under anaerobic conditions, SRB reduce sulfate to sulfide in the sewage. Hydrogen sulfide is released into the aerobic environment at the sewer pipe crown above the sewage where it is oxidized to sulfuric acid by SOB or thiobacilli. Dissolution of the concrete pipe occurs due to the corrosive action of the acid. The probability of MIC increases with increased organics in the sewage, increased temperature, increased sludge, decreased oxygen, decreased flow rate, and decreased drop along the pipe.

Microbiologically influenced corrosion has also been detected in specific types of construction that provide environments for the growth of microorganisms. Davies and Scott (139) reported MIC of support columns for a building in Buffalo, N.Y. The columns were H-shaped ranging in flange thickness from 0.495 to 1.12. in. (12.6 to 28.4 mm) and web thickness between 0.31 and 0.68 in. (7.9 to 17 mm). The columns were originally surrounded with a wet vermiculite–cement fireproofing mix. The corrosion was detected 3 years after construction as blisters on the sheathing of the columns. The corrosion was attributed to the presence and activities of thiobacilli that lowered the pH of the fireproofing mixture and dissolved the concrete.

Posttensioning is a method of reinforcing concrete with highstrength steel strands that keep the concrete in compression. Posttensioning applications include office and apartment buildings, parking structures, slabs-on-ground, bridges, sports stadia, and nuclear power plants. Carbon steel cables used as tendons are typically lubricated with hydrocarbon grease before insertion into preplaced polyvinyl chloride ducts in concrete slabs. Polyvinyl chloride ducts provide corrosion protection and the grease facilitates insertion of the cable into the duct. Cables are posttensioned from one or both ends after the concrete has achieved sufficient strength and anchor plates are attached. Water can be introduced during construction, or can accumulate after construction. Little and co-workers (140) isolated *Fusarium* sp., *Penicillium* sp., and *Hormoconis* sp. from corroding tendons in a posttensioned structure. The pH of the water associated with the corrosion products was consistently 2 or below.

8. Strategies to Prevent or Mitigate MIC

Engineering designs that incorporate drains, eliminate traps for stagnant water, reduce the number of bends and elbows, and specify gasket materials that do not wick, reduce the potential for MIC. Components that typically remain stagnant for long periods of time should be designed to be cleaned or flushed. Where possible, the system design should provide control of the flow velocity that will limit bacterial growth (141). Continuous flow is preferable to intermittent flow. Dead leg and bypass circuits should be avoided wherever possible. Side stream filtration and in-line filters should be included in the design when make-up water contains high levels of suspended solids. Provisions must be made to purge accumulations of suspended solids from the system when it is not possible to prevent their accumulation by insertion of pigs, air bumping, sand-jetting, or high-pressure water spray.

Strategies to mitigate–control the effects of MIC include the following: reduce the numbers and types of organisms in the system or alter potential electron acceptors to inhibit specific groups of bacteria.

8.1. Reduce Numbers and Types of Organism. Numerous methods have been used for minimizing the accumulation of biofilms on engineering surfaces including the following: addition of biocides (oxidizing and nonoxidizing) to the bulk water to kill organisms entering the system or reduce the growth rate of microorganisms within the biofilm, mechanical removal of biofilms from the substratum (sponge balls, brushes), and water treatments to decrease the numbers and types of organisms (aeration, deaeration).

Biocides. A biocide is a product formulated to kill microorganisms. Biocides may be applied as batch doses or as continuous injections or a combination of both. Compatibility with equipment, solubility, dose level, dose frequency, chemical compatibility, safety, persistence, toxicity, cost, and solubility influence the selection and application of a biocide. Several excellent reviews have been written about biofilm and MIC control using biocides (142,143). In all cases, qualification tests are required to ensure that a particular biocide is effective in a particular application. Typical water treatments can disinfect down to 10^3 bacterial counts per milliliter (143). It is well established that it is more difficult to kill bacteria in biofilms with biocides than it is to kill the same types of organisms suspended in a liquid medium because biocides cannot penetrate biofilms (143). Costerton and co-workers (144) report that bacteria in biofilms are resistant to antibiotics and biocides at levels 500–5000 times higher than those required to kill planktonic cells of the same species. There are additional problems with the use of biocides. Persistent use of a single biocide treatment can allow more resistant microorganisms to develop and remain in the biofilm. Ridgway and co-workers (145) demonstrated that bacteria previously exposed to chlorine were more resistant than those never exposed. Resistance to a particular biocide can be overcome by periodically changing the biocide. Numerous investigators have observed a rapid resumption of biofouling after a biocide treatment or mechanical removal of cells from a surface. Regrowth or recovery may be due to the following: (*1*) any remaining biofilm contains viable cells that can reproduce a biofilm; (*2*) the residual biofilm imparts a surface roughness

that enhances transport and sorption; and (*3*) in the case of chlorine, EPS may be preferentially oxidized providing more nutrients (143).

8.2. Alter Potential Electron Acceptors to Inhibit Specific Groups of Bacteria. One practical application for controlling MIC by controlling the electrolyte composition has been used in seawater injection systems. In these systems, seawater is injected into oil reservoirs to maintain pressure. Oxygen is removed to minimize corrosion. However, in the anaerobic environment, growth of SRB is encouraged and corrosion of steel alloys results. Laboratory and field experiments have demonstrated that nitrate treatment can be an effective alternative to biocide treatment. Nitrate addition causes a shift in the microbial population from SRB to nitrate-reducing bacteria (NRB) (146).

Nitrate-reducing bacteria reduce nitrate to N_2 with several possible intermediates, including nitrite. There are several potential mechanisms for the observed inhibition of SRB due to addition of nitrate. One of them is competition for carbon sources. When competing for the same carbon source, NRB outcompete SRB because nitrate is a stronger oxidizer than sulfate. This argument is valid only in carbon-limited waters. Toxic reaction products from the reduction of nitrate to N_2 may inhibit SRB. A shift in the redox potential in the system may also inhibit SRB. As a consequence of nitrate reduction, the redox potential will likely increase, producing unfavorable conditions for sulfate reduction.

Hubert and co-workers (147) demonstrated that both nitrate and nitrite are effective treatments for decreasing sulfide concentrations. The required dose depends on the concentration of oil organics used as the energy source by the microbial community. Because of its higher oxidative power, nitrate can remove more oxidizable oil organics than nitrite. However, nitrite is a strong inhibitor of SRB. Nitrate–nitrite supplementation is a new technology and some work is underway to carefully characterize the bacteria that are developing in nitrate–rich water (148).

It was once thought that sparging a system with air could alleviate corrosion problems due to anaerobes, such as SRB. This idea has since been disproved. Because SRB depend on other organisms to remove oxygen and produce nutrients, they can survive in aerated systems. Aeration will not reduce the impact of SRB and in some cases exacerbates the problem. Altering electron acceptors can also increase the likelihood of MIC. Removing oxygen from seawater has been proposed as a corrosion control measure. Matsuda and co-workers (149) conducted shipboard trials by sealing a ballast tank at the deck and installing vertical pipes into the headspace. They reported that pumping pure nitrogen gas into the headspace for 1.5 h reduced oxygen levels in the seawater to ~0.2 mg/L and decreased the rate of uniform corrosion of carbon steel by 90% as determined by weight loss. However, in laboratory experiments, Lee and co-workers (150) compared corrosion resulting from stagnant aerobic natural seawater with corrosion resulting from stagnant anaerobic natural seawater over a 1-year period. They demonstrated the following: (*1*) corrosion was more aggressive under totally anaerobic conditions as measured by instantaneous corrosion rates ($1/R_p$) and weight loss, (*2*) under aerobic conditions corrosion was uniform and the surface was covered with iron oxides (lepidocrocite and goethite), and (*3*) under anaerobic conditions the corrosion was localized pitting

and the corrosion products were mackinawite and pyrrothite. Lee and co-workers (151) designed field experiment to evaluate deoxygenation of natural seawater as a corrosion control measure for unprotected carbon steel seawater ballast tanks. They demonstrated the difficulty of maintaining hypoxic seawater. By using a gas mixture, it was possible to displace dissolved oxygen. However, aerobic respiration and corrosion reactions consumed oxygen and produced totally anaerobic conditions within the first days of hypoxia. When gaskets and seals failed, oxygen was inadvertently introduced. The impact of oxygen ingress on corrosion depends on the amount of oxygen in the system at the time oxygen is introduced. Carbon steel exposed to cycles of hypoxic seawater and oxygenated atmosphere had higher corrosion rates than coupons exposed to cycles of either consistently aerobic or deoxygenated conditions.

8.3. Corrosion Inhibition by Biofilms. There are numerous reports of laboratory experiments demonstrating corrosion inhibition by biofilms (152–160). Corrosion inhibition due to the presence and activities of bacteria within biofilms has been reported for carbon steel (155) aluminum 2024 (158,161,162), and copper (158). The mechanisms most frequently cited for corrosion inhibition by biofilms are as follows: (*1*) the biofilm forms a diffusion barrier to corrosion products that stifles metal dissolution; (*2*) respiring aerobic microorganisms within the biofilm consume oxygen causing a diminution of that reactant at the metal surface; (*3*) microorganisms produce metabolic products that act as corrosion inhibitors, eg, siderophores; and (*4*) microorganisms produce specific antibiotics that prevent the proliferation of corrosion-causing organisms, eg, SRB.

Apparent contradictions among investigators exist where the same organisms and mechanisms to which MIC has been attributed have also reportedly inhibited corrosion. For example, *Pseudomonas* sp. and *Serratia* sp. are reported to increase the corrosion rate of iron and nickel compared to sterile conditions (163). The same researchers have shown that *Pseudomonas* and *Serratia* can have a protective effect on some metals under some circumstances (153,154). Metal binding by extracellular polymers has been reported as a mechanism for both MIC (164) and for corrosion inhibition (165). There are also problems with the stochastic nature of biofilms, contamination, and natural competition.

Jigletsova and co-workers (166) and Rodin and co-workers (167) carefully examined the influence of environmental conditions on corrosion inhibition by biofilms. They demonstrated that the division of bacteria into ones that caused corrosion and ones that inhibited corrosion was entirely arbitrary. They demonstrated that the corrosive properties of biofilms varied with culture conditions. Dubiel and co-workers (168) concluded that the physiology of the bacteria in the biofilm, the flow rate and the chemistry of the electrolyte determine the ultimate impact of microorganisms on corrosion.

Despite the laboratory studies indicating possibilities for using bacteria to inhibit corrosion of a number of alloys, applications have not been successful (169). The following critical issues must be addressed before bacteria can be used to predictably inhibit corrosion: (*1*) the stochastic nature of biofilms, (*2*) contamination, and (*3*) natural competition.

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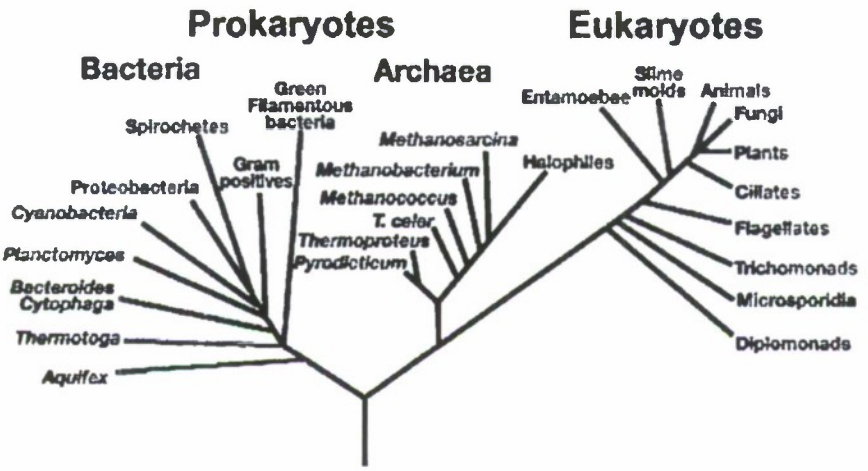

Fig. 1. Phylogentic tree of life illustrating the three main branches of microorganisms: bacteria, archaea, eukaryotes.

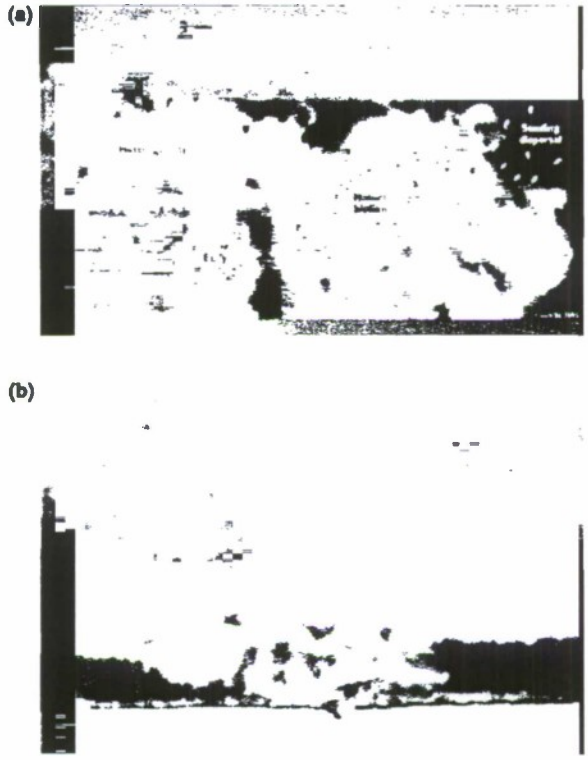

Fig. 2. (a) Conceptual illustration of the heterogeneity of biofilm structure and function. Foreground: biofilm life cycle. Mid-ground: heterogeneity in bacterial activity and communities make-up. Background: Streamer formation and detachment (11). [Reprinted with permission from P. Dirckx Center for Biofilm Engineering, Montana State University, Bozeman]. (b) Light microscope image of a cross-section through a mixed culture biofilm on a corroding carbon steel surface. [Reprinted with permission of Dr. Z. Lewandowski, Center for Biofilm Engineering, Montana State University.]

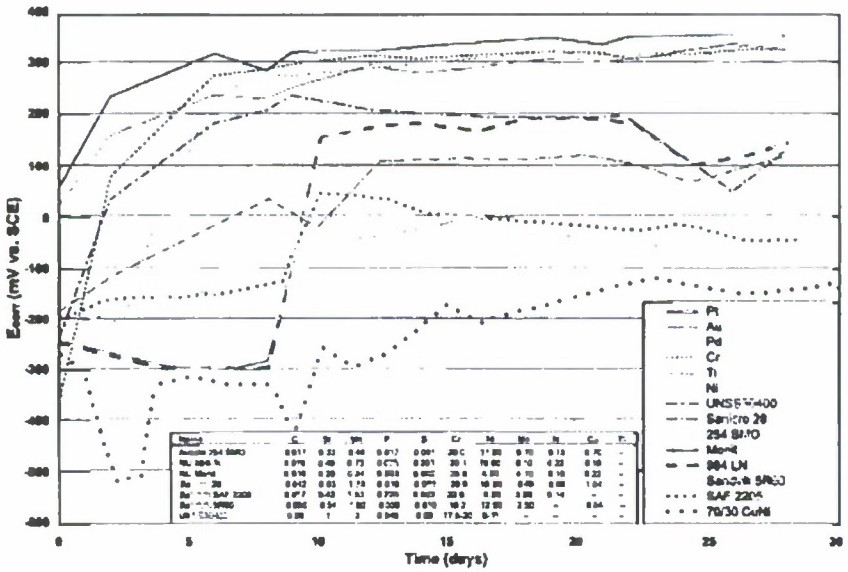

Fig. 3. Composite of E_{corr} vs. time data (15–17) for materials exposed in natural seawater.

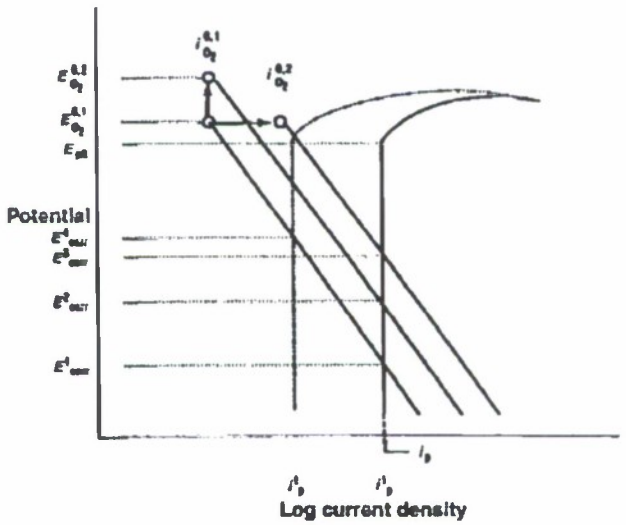

Fig. 4. Schematic polarization curves for stainless steel in seawater (19).

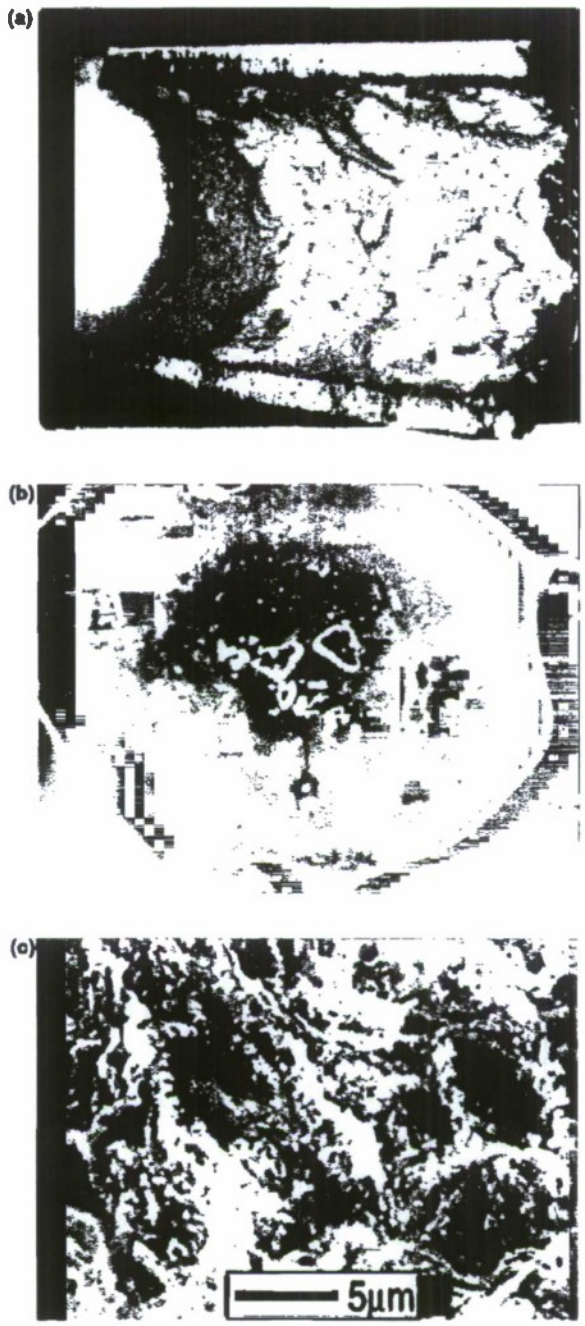

Fig. 5. (a) Tubercles on galvanized steel tube. (b) Tubercle in a defect on a coated carbon steel surface. (c) Environmental SEM of twisted sheaths of iron-oxidizing bacteria typically found in tubercles.

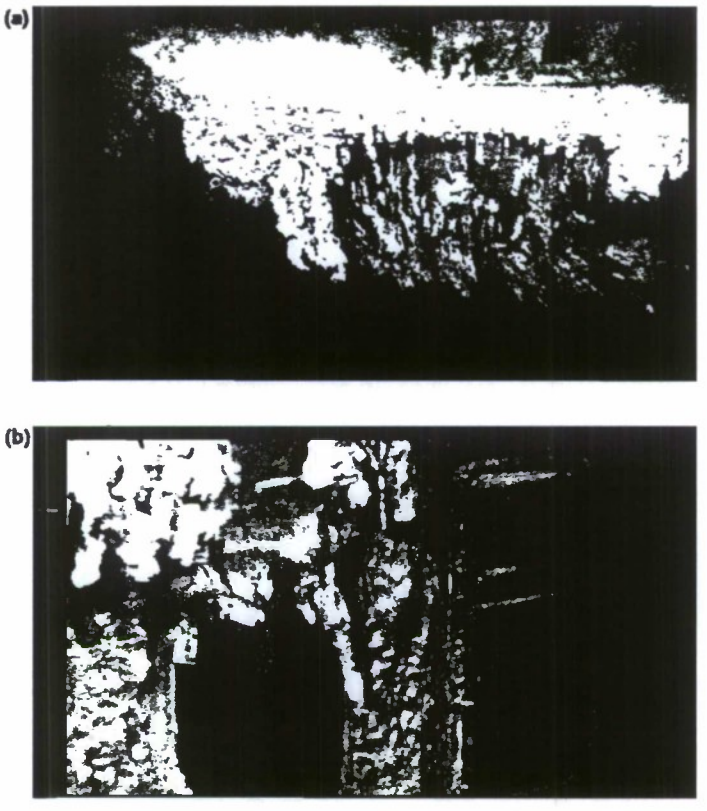

Fig. 6. (a, b) Rusticles on the RMS *Titanic*. [Courtesy of The Institute for Exploration, Mystic, CT].

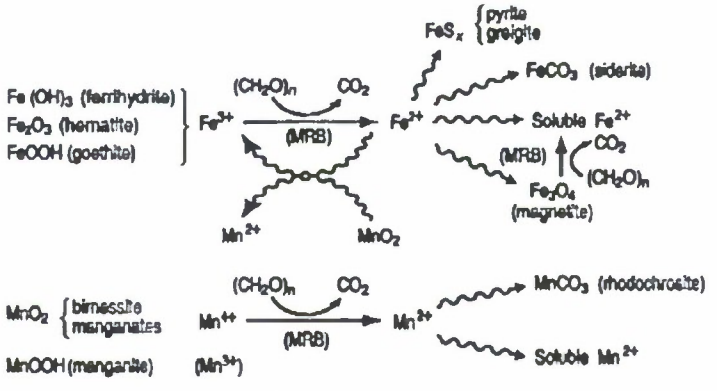

Fig. 7. Possible reactions of iron and manganese oxides mediated by MRB in anoxic conditions (62).

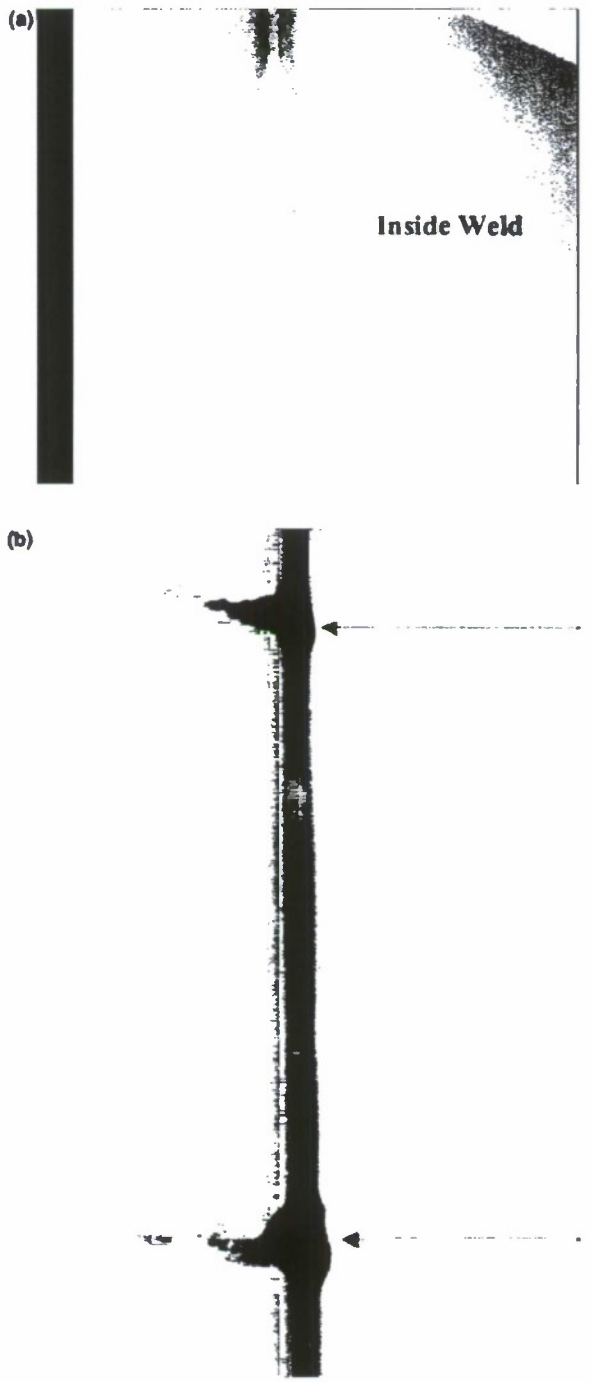

Fig. 8. (**a**) Vertical weld in 316L stainless steel exposed to stagnant natural seawater for 8 weeks. Iron-oxidizing bacteria were associated with corrosion products. (**b**) X-ray micrograph of failed vertical weld in 316L indicating pitted areas (95).

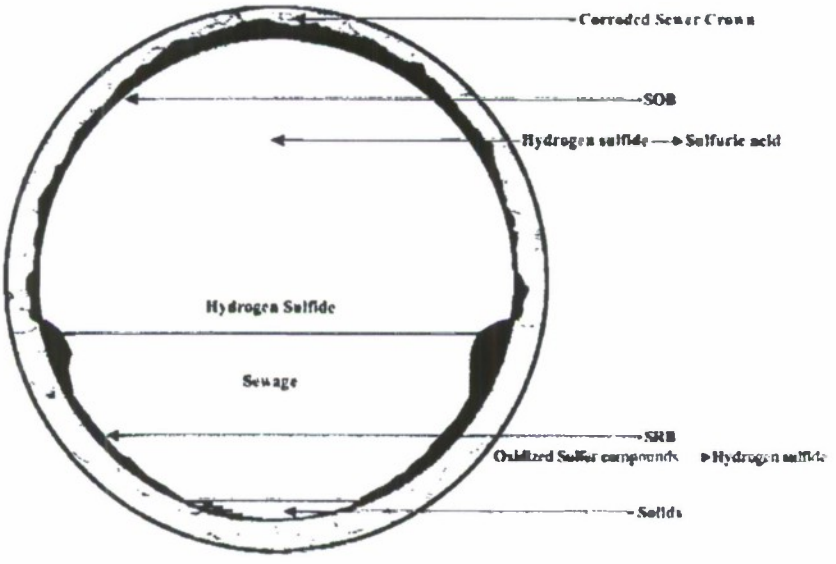

Fig. 9. Schematic of sulfur cycle in concrete sewer, resulting in corrosion at sewer crown.

Table 1. **Iron Oxidizing Bacteria Associated with Tubercles or Rusticles (49).**

Structure	Exposure conditions	Electrolyte	Mineralogy	Organism	References	Details
Titanic carbon steel	Atlantic Ocean 3800 m 1°C 6000 psi	seawater	geothite lepidocrocite	*Leptothrix ochracea*	53,54	rusticles
SS Central America carbon steel	North Atlantic 2,000 m 5.6 $mgL^{-1}O_2$ 35% salinity	seawater		*Leptothrix ochracea and Siderocapsa, leptothrix dicophora*	58	rusticles
USS Monitor wrought iron	Atlantic Ocean 240 ft.	seawater	outer shell—siderite, lepidocrocite and goethite innercore—magnetite	IOB were not specifically identified	60	rusticles
Pilings carbon steel	Lake Superior	freshwater	under investigation	*Siderooxidans lithoautotrophicus*	48	tubercles
Water tank 316L stainless steel	ambient	drinking water			5	tubercles
304L stainless steel	ambient	brackish water and untreated well water		*Gallionella*	49	tubercles

Table 2. **Chemical Compositions of Nickel-Based Alloys (wt%) (104).**

Alloy	Ni	Cu	Cr	Fe	Mn	C	Si	S	Co	Mo	W	Nb	Ti	Al	V
400	63.0 min	28.0–34.0		2.5	0.2	0.3	0.5	0.024							
625	58.0 min		20.0–23.0	5.0	0.5	0.1	0.5		1.0	8.0–10.0		3.15–4.15	0.4	0.4	
C-22	Bal.		20.0–22.5	2.0–6.0	0.5	0.015	0.08		2.5	12.5–14.5	2.5–3.5				0.35

Table 3. **Chemical Compositions of Stainless Steels (wt%) (104).**

	C	Cr	Mn	Si	Ni	P	S	Mo	Cu
304	0.08	18.0–20.0	2.0	1.00	8.0–10.5	0.045	0.03		
304L	0.03	18.0–20.0	2.0	1.00	8.0–12.0	0.045	0.03		
308	0.08	19.0–21.0	2.0	1.00	10.0–12.0	0.045	0.03		
316L	0.03	16.0–18.0	2.0	1.00	10.0–14.0	0.045	0.03	2.0–3.0	
410	0.15	11.5–13.5	1.00	1.00		0.04	0.03		
904L	0.02	19.0–23.0	2.00	1.00	23.0–28.0	0.045	0.035	4.0–5.0	1.0–2.0

Table 4. **Chemical Compositions of Antimicrobial Metals (wt%) (120).**

Sample	C	Si	Mn	P	S	Cr	Ni	O	Ag
silver alloyed	0.054	0.43	1.0	0.037	0.004	18.50	8.00	0.0062	0.039
silver coated	0.042	0.26	1.03	0.035	0.003	18.34	8.30	0.0040	<0.001